PB-229 105

A STUDY OF ORGANIC CONTAMINANTS IN BOUNDARY WATERS USING CARBON FILTER TECHNIQUES, LAKE HURON-LAKE ERIE, 1953-1955

F. M. Middleton, et al

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

September 1956

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PERSONNEL PARTICIPATING IN THIS SURVEY WERE:

United States

H. H. Black, In Charge, Industrial Waste Studies
F. W. Kittrell
F. M. Middleton
R. H. Burttschell
A. A. Rosen
H. H. Pettit

Canada

A. V. DeLaporte
J. Binkiewicz
A. Harris
B. Boyer
R. Tait

Acknowledgment

The excellent cooperation of water works personnel at the various plants studied is gratefully acknowledged.

September, 1956

Report prepared by: F. M. Middleton
A. V. DeLaporte

RESUME AND EVALUATION OF CARBON FILTER STUDIES ON BOUNDARY WATERS

Lake Huron - Lake Erie

It was the purpose of this survey to recover and identify organic contaminants in the Boundary Waters by means of carbon filter sampling methods and organic analyses and to assess these materials as potential causes of taste and odor in drinking water supplies.

Results:

1. A concentration of 25 to 50 micrograms per liter (parts per billion - P.P.B.) of chloroform extractable organic materials was found to be common to these waters and probably represents conditions which would rarely give rise to troublesome taste and odor problems.

2. Very significant differences in the concentrations of materials occurred between 1953 and 1955. Concentrations of organics as high as 980 p.p.b. were found in 1953. An oily contaminant was responsible for the large concentration. Many of these materials survive water treatment and are found in the finished water in concentrations only slightly less than in the raw water.

3. Most of the chemicals found either represent natural materials or the end products of natural purification on the industrial contaminants of the waters.

4. Non-natural components found include:

a. DDT in concentrations of approximately 5 p.p.b. in 1953 at Mt. Clemens and Wyandotte.

b. Light, oily materials containing aliphatic hydrocarbons and aromatic materials of the toluene and xylene types. This material may originate from wash-in of solvents used for insecti-

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cide dispersions or from other sources presently unknown. These materials were not observed on the Canadian side.

c. An aromatic chemical, believed to be diphenyl oxide (phenyl ether) was found on the Canadian side at Corunna and Wallaceburg. The concentration was not sufficient to be of great significance but such findings aid in tracing pollution and alerting authorities to other possibilities.

5. The neutral components of the material recovered from the water were most odorous by laboratory test. Water containing more than 50 to 100 p.p.b. of total organics (the neutrals are usually 50% or more) would be expected to be a potential taste and odor hazard.

6. Phenolic materials during the time of this survey appeared to be of relatively minor significance as causes of taste and odor compared to the possible contribution of other materials. Accidental spills or careless discharges of phenol may, of course, cause objectionable conditions.

Future Use of Carbon Filter:

The results have indicated the usefulness of the carbon filter to assess the quality of these waters regarding organic content and contaminants. No other way is known to obtain this information. Future uses of this method on these waters might include:

a. Monitoring the organic content and changes at selected locations on both sides of the boundary. This procedure would provide further basic data on these waters and permit the detection of significant pollutional changes due to industrial contamination. Long term studies of waters above all pollutional sources would establish the concentration of organics which

are due to nature.

b. The method could be used for direct industrial waste tracing. This would include studying significant effluents and the stream at intervals below the discharge to determine the total effect of specific pollution.

GENERAL INFORMATION

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1954-55 Study:

The objective of this study was to recover organic contaminants from the waters on both sides of the boundary simultaneously and to identify the materials which may be responsible for causing objectionable tastes and odors in water supplies in the area. Carbon filter studies on the United States side had been made previously and the results have been reported.

This report will present the results of the 1954-55 studies and will review and include data from previous reports of carbon filter studies to bring all of the available information together under one cover. Carbon filter sampling is a specialized technique. The details of the method of analysis of materials recovered from the filters will be found in the Appendix.

Sampling Points:

Carbon filters were operated from December 1954 to April 1955 at Detroit and Mt. Clemens on the United States side and at Point Edward, (water from Lake Huron) Corunna, (about 8 miles below Sarnia) Wallaceburg and Windsor on the Canadian side. Untreated water was sampled in every case.

QUANTITIES OF MATERIALS RECOVERED

The chloroform soluble materials are usually most significant as causes of tastes and odors and chloroform is the most common solvent used in eluting the materials from the carbon. Tables 1 and 2 show the amounts of such materials recovered from the carbon filters used on the waters at the various locations. At Detroit and Windsor recoveries ranged from 25 to 58 parts per billion (p.p.b.) These concentrations of materials are

probably normal to these waters and do not represent high levels of contamination. Higher concentrations (41 to 167 p.p.b.) of organics were found at Mt. Clemens and at Wallaceburg (53 to 69 p.p.b.). At Corunna the one sample taken had a concentration of 76 p.p.b. of organics while at Point Edward 35 p.p.b. of organics were recovered.

The concentration of materials recovered is low compared to recoveries obtained in 1953 when 715 to 980 p.p.b. of organics were recovered from Mt. Clemens. Wyandotte water at the same time yielded 164 to 605 p.p.b. of materials (See Appendix for detailed tabulation).

Figures 1 and 2 show in chart form the recoveries from raw water and a comparison of recoveries from raw and finished water.

KINDS OF MATERIALS RECOVERED

The concentrated materials recovered from the carbon consisted of dark brown waxy or semi-liquid substances. In addition the samples from Mt. Clemens had an oily layer on top of the waxy material equal to 10 to 65 per cent of the total sample. The Detroit samples had less than 5% of the oil. Samples collected in 1953 contained large quantities of similar oily materials. No oily layers were observed in the samples collected from the Canadian side.

The oil, light yellow in color, appears to be a refined material of petroleum origin, but does not appear to be associated with refinery wastes. The odor is like that of fly-spray or at high dilution it is kerosene-like. Upon steam distillation of the oily layer, 68% of the material was recovered in the first 12 ml. of condensate. The infrared spectrum (Fig. 3) of this material indicated it to be a mixture of aliphatic and aromatic hydrocarbons. Some of the possible components of an aromatic nature are toluene and xylene mixtures. Such materials may be used as solvents and as ve-

hicles for spraying insecticides. In 1953 DDT was recovered along with the oily materials from the Boundary waters. There was no evidence of DDT in the samples collected in 1954-55.

While oily materials similar to those recovered at Mt. Clemens were not found on the Canadian side a specific pollutant was revealed. Infrared spectra of aromatic fractions of the neutral groups (See appendix for separation procedures) from samples on the Canadian side showed an interesting pattern of pollution. At Point Edward no specific identification could be made from the aromatic fraction. At Corunna the aromatic fraction, based on the infrared spectrum, appeared to be almost all phenyl ether (also called diphenyl ether or diphenyl oxide). The principal infrared absorption bands of the sample and pure phenyl ether are compared in the following table.

	Wave Length - Microns								
Aromatic Fraction from Corunna	5.2	6.3	7.5	7.8	8.1	8.3	8.6	9.3	9.75
Pure Phenyl Ether	5.2	6.2	7.5	7.8	8.1	8.4	8.6	9.3	9.75

The excellence of the comparison is very strong evidence that the material is phenyl ether. This material also appeared at Wallaceburg but in diminished amounts and at Windsor the chemical had disappeared. Figure 4 shows the critical portions of these spectra at the various sampling points and indicates an interesting pollutional pattern. Phenyl ether is a by-product in the Dow process for the manufacture of synthetic phenol. The exact source of the material in the Corunna sample was not established.

The following recoveries from the various Canadian aromatic fractions are of interest.

Location	Aromatics Recovered P.P.B.
Point Edward	1.0
Corunna	10.1
Wallaceburg	5.8
Windsor	2.2

Odor tests were not made on these fractions but tests on pure phenyl ether made in the SEC laboratories indicated it to have a threshold odor of 13 p.p.b. It should be pointed out that recoveries from the carbon filter tend to be less than 100% so that somewhat greater concentrations of materials actually exist than those recorded. It is probable that the material was present in threshold amounts in the raw water.

A portion of the chloroform extract of selected samples was separated into chemical groups as follows: ether insolubles, water solubles, weak acids (includes phenols), strong acids, bases and neutrals. The neutrals may be further separated by chromatography into aliphatic, aromatic and oxygenated materials. Tables 3, 4, and 5 shows the amounts recovered and the percentage of each constituent present.

Although the listed groups are still complex some interpretation can be made as to the possible origin and effect of the materials. The following discussion represents a brief interpretation of the meaning of the results recorded in Tables 3, 4, and 5.

Total Extract:

The total amount of material recovered is useful for comparative purposes among the various sampling points. Unusual happenings and differences in the water from season to season and year to year are reflected in the results. Visual inspection and gross odor may reveal something of

the nature of the material but further separation is usually necessary if further characterization of the material is desired.

Ether Insolubles:

These are tarry or polymerized materials which do not dissolve in ether. Nearly all taste-and-odor-bearing materials are soluble in ether and prefer this solvent to water. Very few ether insolubles were found in these waters.

Water Solubles:

When an ether solution of the recovered organic materials is mixed with water some of the compounds prefer the water and partition into the water phase takes place. These are the water solubles. Again these materials are not usually significant as odor bearers although they make up a substantial portion of the total extract. It is probable that they are mostly acidic substances and originate from nature or sewage.

Weak Acids:

Phenols and other weakly acidic substances along with more strongly acidic substances are put into dilute sodium hydroxide in which solution the sodium salts formed are soluble. The weakly acidic materials are weaker than carbon dioxide and may be freed from the sodium hydroxide by passing CO_2 gas into the sodium hydroxide solution. An ether extraction removes these weak acids and they are recovered. Phenols, known for their taste and odor effects, occur in this group but they are usually a very minor constituent of the total group in most waters.

Strong Acids:

If the solution remaining after removal of the weak acids (essentially a weak bicarbonate solution) is acidified with hydrochloric acid the remaining strong acids are freed and can be recovered by ether extraction. These are principally carboxylic acids. Such materials may be natural to

water or they may represent partial oxidation products of industrial materials. There is no practicable way of differentiating the source of such materials at present. The materials are highly odorous and generally constitute a substantial portion of the recovered materials.

Bases:

These are organic amines. Such compounds are known for their odorous characteristics. However, very little of the amines have been recovered from most waters. Exceptions would be near a plant discharging quantities of such materials. As found in the Boundary waters by the methods used, they do not appear to be significant.

Neutrals:

As the name states these materials are neither acidic nor basic. Being neutral the chemical activity is less than other materials and the materials are more resistant to attack by natural purification forces. Hydrocarbons such as the oily materials recovered are examples of neutral compounds. Many oxygenated compounds such as aldehydes, ketones, esters and ethers are also in this group. Usually, the materials comprise the largest percentage of the total materials and are very odorous.

Aliphatics, Aromatics and Oxys:

Separation of the neutral materials by chromatographic means yields the three above named sub-groups. Aliphatic materials are represented by common mineral oil, aromatics by benzene and the oxys as stated above are aldehyde, ketones, etc. In a water containing old pollution nature may have converted most of the materials into some form of oxidized substance and the percentage of oxys is usually highest in such waters. In the case of the oil pollution, however, the aliphatic and aromatic ma-

erials exceed the oxys and provide substantial evidence of recent pollution or of very stable materials. Hence an examination of the relative proportions of the three sub-groups of the neutrals may reveal something of the waters' history.

Loss:

Losses occur in separating the original materials and in the chromatographic step. These losses are partially inherent in manipulations of the kind required to carry out the procedure. Such loss would not usually be more than 10 or 15%. Larger losses are probably due to volitilization of the lower boiling materials that may be in the water. In general, the highly volatile materials may be lost before the water is delivered to the consumer.

Results of the interpretation of infrared absorption spectra are useful, but the complexities of the waxy portion of these samples make the exact identification difficult. The following is the interpretation of samples from the Canadian side:

General:

The graphs represent the complex mixture of a very large number of chemical compounds and the bands for individual compounds are overlapping. This makes it difficult to identify individual compounds, although separation of chemical groups is satisfactory. Chromatography seems to be a good method for the separation of neutral groups of all three fractions; aliphatics, aromatics and oxy compounds do not show the contamination with solvents used.

Aliphatics:

The compounds with long carbon chains are prevailing and no drastic change in the length of chains is indicated by graphs when the water flows down to Windsor. It seems that aliphatic

compounds do not undergo much change when once discharged to the river, anyway not between Sarnia and Windsor. At Point Edward the carbon chains seem to be shorter.

Aromatics:

Rather strongly substituted aromatic rings are prevailing. Possible chlorobenzene. No chlorophenol, no phenol, no styrene are found in this fraction. Aromatic compounds are much quicker destroyed in river water than aliphatics. Graphs for Windsor show only small contamination with aromatics.

Oxy compounds:

OH, C = C, and C = O groups are present here. Possible ketones and hydroxyketones. Carbonyl group is more prominent at Windsor than at Corunna.

Weak Acids:

Hydrogen bonded OH group and carbonyl group very prominent. Large amount of fatty acids; metallic soaps found at Wallaceburg are gradually decomposed along the river, Phenol found at Wallaceburg but not at Windsor. Possible amino-acids.

Strong Acids:

OH group not so strongly hydrogen bonded as on the previous fraction. (Fatty acids present also metallic soaps).

Amines:

No evidence for primary amines and aminohydrochlorides. Possible higher amines.

Water Soluble:

Much more CH_3 groups present. Compounds in this fraction are rather of shorter carbon chains. Probably short chain aldehydes and ketones of aliphatic character are prevailing here.

ODOROUS CHARACTERISTICS

The odorous characteristics of 3 samples of carbon filter extract on the American side were studied. Time did not permit studies of the odorous properties of the Canadian samples. Extensive testing of odor and taste characteristics did not reveal any serious difficulties during the survey period.

Table 6 shows the p.p.b. of the various materials which were detected by odor and taste tests. Panels of 3 to 6 people observed each sample and the value reported is the geometric mean of the observations. Sample 482 was collected at a time when no perceptible odor or taste was noted in the raw water. The other samples were collected at times of some taste and odor but not under severe conditions. The raw extracts had odor concentrations from 10 p.p.b. to 150 p.p.b. In addition to odor tests the samples (492 and 493) were tasted in their normal state and after chlorination (0.1 p.p.m. residual chlorine after 15 minutes contact). The taste threshold on sample 492 (Detroit) was 1000 p.p.b. compared to an odor threshold of 120. Chlorination did not change the taste threshold. Sample 493 (Mt. Clemens) had an odor threshold of 10, a taste threshold of 150 and a chlorinated taste threshold of 15. The amino group may be disregarded as an odor contributor due to the very small quantities present and the relatively higher thresholds. The strong and weak acids are significant from the standpoint of potential odor and taste causing compounds. Phenolic materials if present would be in the weak acid fraction. The threshold taste of the weak acid fractions was lowered by chlorination but not in an extreme manner such as is encountered when free phenol is chlorinated. The neutral materials were lowest in odor threshold. Taste thresholds were higher than odor

thresholds. Chlorination did not affect the taste thresholds of the neutral materials.

To obtain the relative odor contribution of the various groups separated a weighting factor termed ODOR ABUNDANCE is used. This factor is computed as follows:

$$\text{ODOR ABUNDANCE} = \frac{\% \text{ of Group Present} \times 1000}{\text{Threshold Odor Concentration in p.p.b.}}$$

Table 7 presents data showing the relative contribution to odor of the various groups. It will be noted that the neutral materials are by far the largest contributors of odor with the acid fractions next. Water solubles and amines do not appear important even though the water solubles constitute a large proportion of the total extract. Further separation of the neutral materials indicates that the materials consist of 70% or more oxygenated materials and the remainder aliphatic and aromatic hydrocarbons. The oxygenated materials are strongly odorous.

General odor conditions in the lake and river at the time of sampling on this study were very good. Details have been reported in the April 1955 report to the Commission. Some sporadic tastes and odors of low level occurred but no prolonged difficulties were experienced.

These results do not preclude the presence of phenol in small concentrations at irregular intervals which may produce taste and odor problems. They do indicate that many other materials are present in much greater concentrations and that an odor and taste causing potential is present.

Since odor tests were not made on the Canadian samples no estimate can be given of the odor potential of the materials recovered. However, since recoveries were low, it would not be expected at the time of this survey that objectionable conditions would be present.

SUMMARY

1. Concentrations of chloroform extractables recovered were as follows:

American Side		Canadian Side	
	parts per billion		
Mt. Clemens	41 - 167	Pt. Edward	35 (1 sample)
Detroit	41 - 58	Corunna	75.5 (1 sample)
		Wallaceburg	53 - 69
		Windsor	23 - 39

These recoveries are significantly lower than those obtained in these waters in 1953 when Mt. Clemens had 715 to 980 p.p.b.

2. The materials recovered at Detroit could be detected in odor-free water when present in approximately 100 p.p.b. or more. Hence odorous conditions would not be expected since concentrations of less than this were actually recovered. The chemicals recovered from the Mt. Clemens raw water could be detected at concentrations of 10 p.p.b. Effective water treatment was apparently successful in moving these materials since odorous conditions were not severe during the sampling period. The neutral group was the principal odor contributing portion of the filter extract.

3. The bulk of the materials recovered on both the American and Canadian sides appeared to be of natural origin or represented stable oxidation products of industrial materials. This was particularly true at Detroit and Windsor. Non-natural pollutants were found at Mt. Clemens in the form of a light oil, probably a solvent, and evidence of aromatic materials (believed to be principally phenyl ether) appeared at Corunna and Wallaceburg.

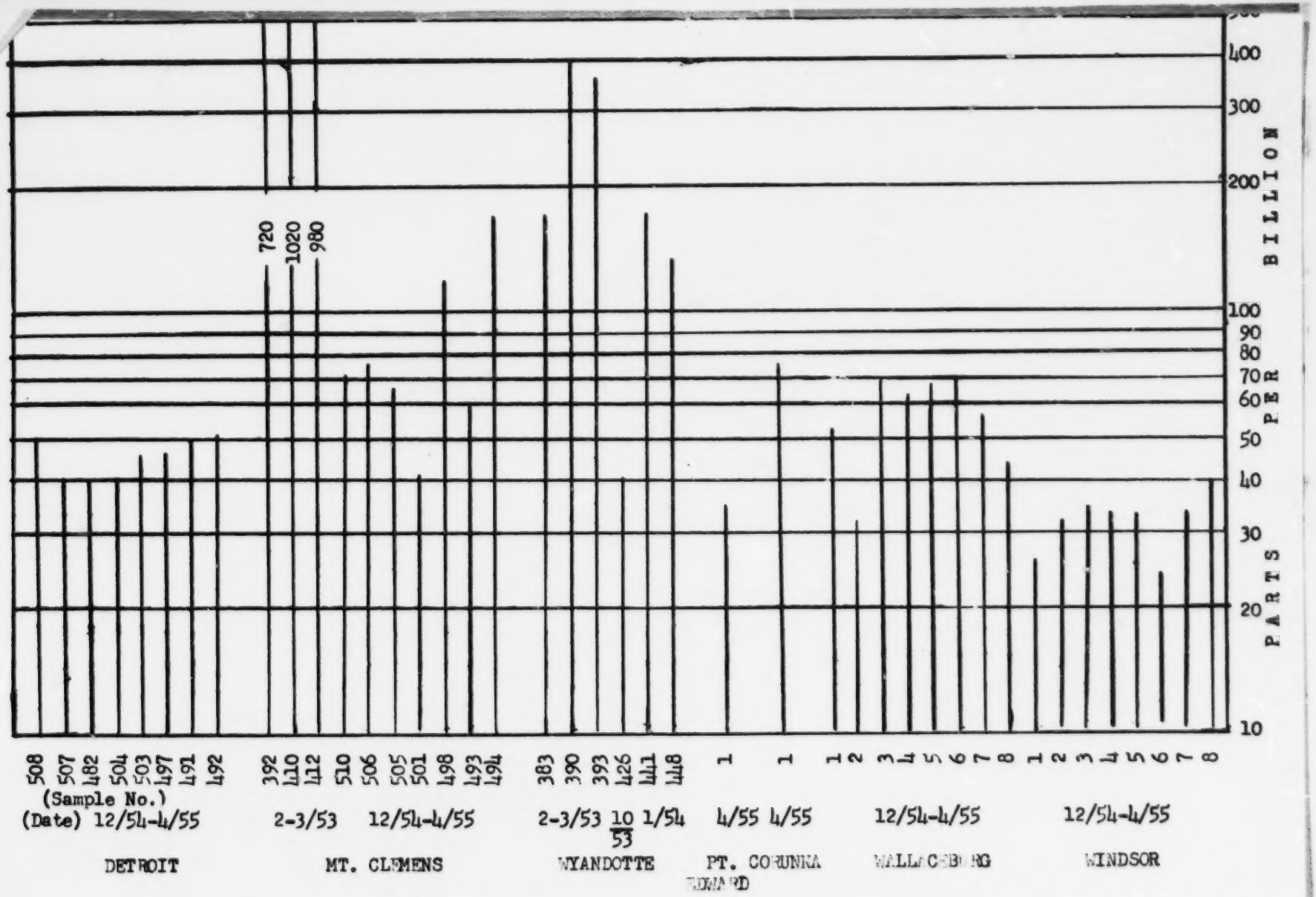


Figure 1. Chloroform Extractable Organics Recovered from Raw Waters

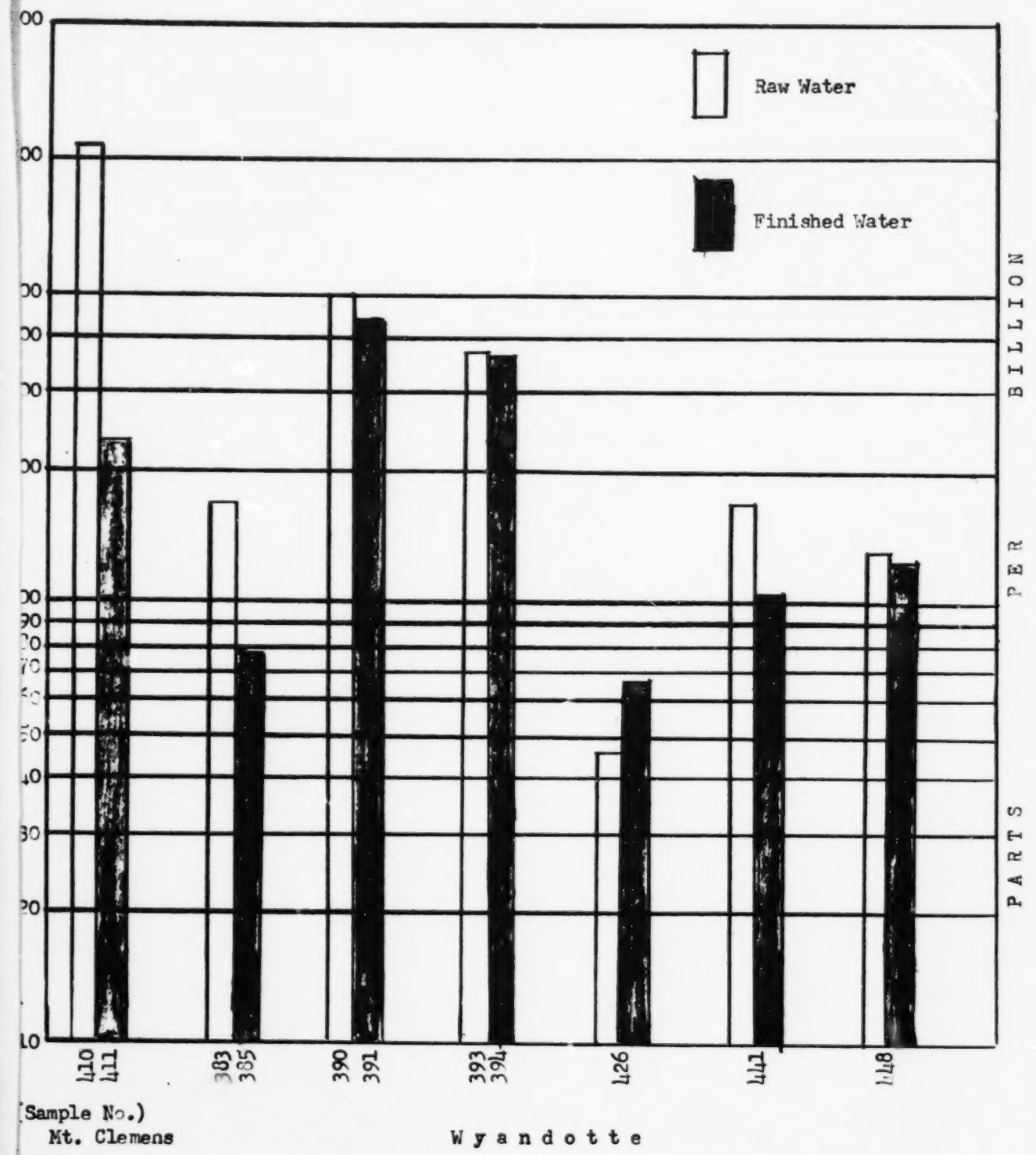


Figure 2. Comparison of Organics Recovered from Raw and Finished Water.

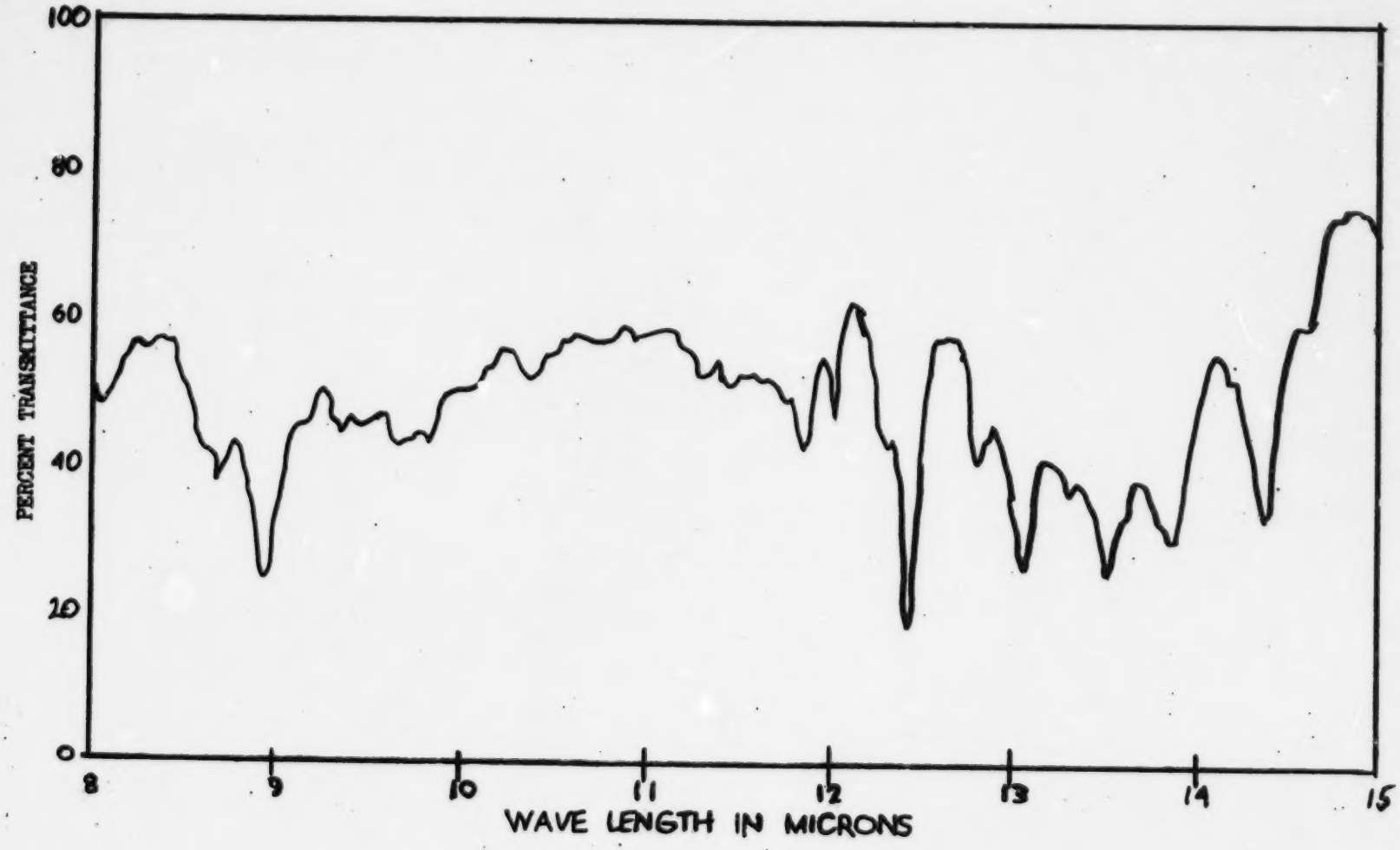
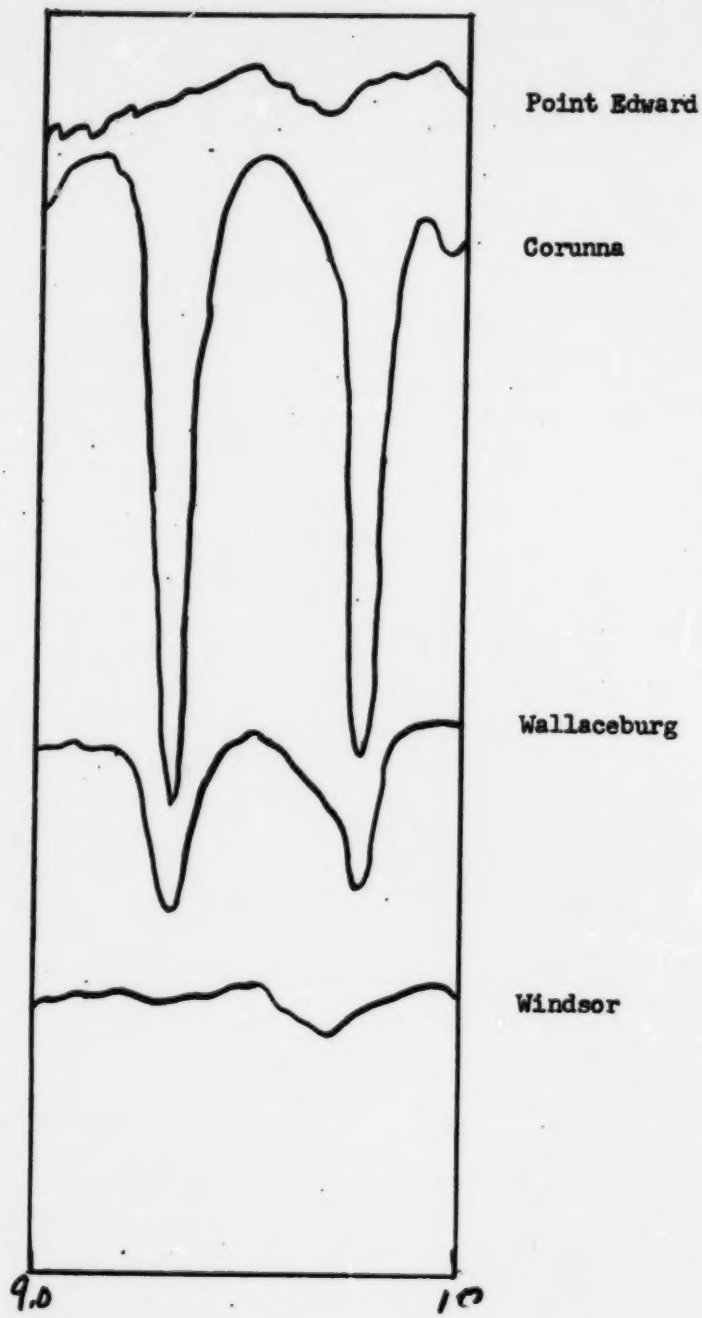


Figure 3. Infrared Spectrum of Steam Distillate of Oily Layer

Mt. Clemens, Michigan



Wave Length in Microns

Figure 4. Infrared Spectra of Aromatic Fractions Between 9.0 and 10.0 Microns

Table 1

BOUNDARY WATER SURVEY 1954 - 55 LAKE HURON - LAKE ERIE

Chloroform Extractable Materials Recovered from Raw Water by Carbon Filter

Mt. Clemens, Mich.			Detroit, Mich.		
Dates of Filter Operation	Sample No.	P.P.B.	Dates of Filter Operation	Sample No.	P.P.B.
12/16/54 12/30	510	70	12/1/54 12/17	508	51
12/30 1/13/55	506	74	12/17 12/31	507	41
1/13 1/27	505	64	12/31 1/14/55	482	58
1/27 2/10	501	41	1/14 1/28	504	41
2/10 2/23	498	115	1/28 2/11	503	47
2/24 3/10	493	71	2/11 2/25	497	47
3/10 3/26	494	167	2/25 3/11	491	50
			3/11 3/25	492	52

Table 2

BOUNDARY WATER SURVEY 1954 - 55 LAKE HURON - LAKE ERIE

Chloroform Extractable Materials Recovered from Raw Water by Carbon Filter

CANADIAN SIDE

	Dates of Filter Operation	Sample No.	P.P.B.
Pt. Edward	4/7/55 4/21	1	34.9
Corunna	4/7/55 4/22	1	75.5
Wallaceburg	12/1/54 12/16	1	52.7
	12/16 1/4/55	2	30.6
	1/4 1/13	3	68.5
	1/13 1/21	4	58.0
	1/27 2/10	5	64.1
	2/10 2/22	6	67.2
	2/24 3/10	7	55.9
	3/10 3/24	8	42.9
			54.9

	Dates of Filter Operation	Sample No.	P.P.B.
Windsor	12/4/54 12/17	1	25.4
	12/17 1/4/55	2	32.2
	1/4 1/14	3	33.7
	1/14 1/28	4	32.0
	1/28 2/11	5	32.8
	2/11 2/25	6	23.3
	2/25 3/11	7	32.7
	3/11 3/24	8	39.8
			31.6

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Table 3

BOUNDARY WATER SURVEY 1954 - 55 LAKE HURON - LAKE ERIE

Organic Components Recovered from Raw Water

UNITED STATES

Sample No.		Total Extract (Chloroform)	Ether Insoluble	Water Soluble	Weak Acids	Strong Acids	Bases	Neutrals	Loss	Neutrals			
										Aliphatic	Aromatic	Oxy.	Loss
	Mt. Clemens												
498	P.P.B.	115	-	37.0	9.7	14.3	1.0	24.5	28.5	2.4	2.7	17.3	2.3
	%	-	-	42.8	11.2	16.5	1.2	28.3	24.8	10.6	11.9	77.5	9.5
493	P.P.B.	71	-	31.3	10.4	9.9	1.6	64	15.7	12.1	3.5	35.0	13.5
	%	-	-	26.7	8.9	8.4	1.4	54.6	11.8	24.0	6.9	69.1	21.1
494	P.P.B.	167	-	40.7	9.0	14.2	0.5	66.6	36.7	-	-	-	-
	%	-	-	31.3	6.9	10.9	0.4	50.4	22.0	-	-	-	-
	Detroit												
482	P.P.B.	58	-	20.2	2.7	2.5	0.8	11.3	20.5	-	-	-	-
	%	-	-	54.0	7.1	6.7	2.1	30.1	35.5	-	-	-	-
497	P.P.B.	47	-	16.4	2.4	4.7	2.4	9.9	12.4	1.0	1.0	6.8	1.2
	%	-	-	48.7	7.2	13.9	0.7	29.4	26.9	11.5	11.0	77.6	12.2
491	P.P.B.	51	-	16.1	4.2	6.0	0.8	15.5	7.7	-	-	-	-
	%	-	-	38.4	9.6	13.8	1.8	36.3	15.1	-	-	-	-
492	P.P.B.	52	-	20.4	4.9	4.8	0.4	16.7	5.8	1.8	1.7	12.2	-
	%	-	-	43.2	10.3	10.2	0.9	35.3	11.0	11.2	10.9	77.9	-

Table 4

BOUNDARY WATER SURVEY 1954 - 55 LAKE HURON - LAKE ERIE

Organic Components Recovered from Raw Water

CANADA

Sample No.		Total Extract (Chloroform)	Ether Insoluble	Water Soluble	Weak Acids	Strong Acids	Bases	Neutrals	Loss	Neutrals			
										Aliphatic	Aromatic	Oxy.	Loss
	Pt. Edward												
1	P.P.B.	34.9	1.75	6.9	2.9	4.1	0.45	13.0	5.8	0.7	1.0	9.3	2.0
	%	-	5.0	19.2	8.4	11.9	1.3	37.4	16.8	5.3	7.9	71.6	15.2
	Corunna												
1	P.P.B.	75.5	-	7.3	Lost	Lost	1.1	38.1	-	8.3	10.1	18.9	0.8
	%	-	-	9.7			1.5	50.5	-	21.7	26.5	47.1	4.7
	Wallaceburg												
1	P.P.B.	52.7	-	6.2	7.0	5.3	1.2	28.6	4.3	8.2	5.1	14.7	0.6
	%	-		11.7	13.3	10.1	2.3	54.4	8.2	28.5	17.8	51.6	2.1
2	P.P.B.	30.6	-	3.2	2.0	3.9	0.2	18.1	3.2	4.7	2.8	8.8	1.8
	%	-		10.3	6.6	12.8	0.6	59.4	10.3	26.2	15.5	49.3	10.0
3	P.P.B.	68.5	6.0	25.1	1.4	5.8	0.55	24.3	5.4	7.3	4.4	12.5	0.1
	%	-	8.8	36.6	2.1	8.4	0.8	35.4	7.9	29.9	18.2	51.5	0.4
4	P.P.B.	58.0	-	12.3	6.2	5.9	0.64	22.1	10.8	6.1	6.4	9.6	0.02
	%	-		21.5	10.7	10.1	1.1	38.0	18.6	27.6	28.8	43.5	0.1
5	P.P.B.	64.1	1.1	9.1	6.0	4.7	0.6	35.2	7.4	-	-	-	-
	%	-	1.6	14.2	9.3	7.4	1.0	54.9	11.6				

Table 4 (Cont'd)

Sample No.		Total Extract (Chloroform)	Ether Insoluble	Water Soluble	Weak Acids	Strong Acids	Bases	Neutrals	Loss	Neutrals			
										Aliphatic	Aromatic	Oxy.	Loss
	(Wallaceburg)												
6	P.P.B.	67.2	-	9.5	2.3	8.1	1.3	37.0	9.0	10.2	8.7	18.0	0.1
	%	-		14.2	3.4	12.1	2.0	55.0	13.3	27.8	23.6	48.5	0.1
7	P.P.B.	55.9		11.1	4.0	5.2	0.5	27.1	7.9	0.2	4.9	22.0	-
	%	-	0.1	19.9	7.1	9.3	0.9	48.5	14.2	0.7	18.2	81.0	0.1
8	P.P.B.	42.9	-	7.5	3.9	8.4	0.78	19.5	2.8	3.5	3.2	8.8	4.0
	%	-		17.6	9.2	19.7	1.8	45.3	6.4	18.1	16.3	45.1	20.4
	P.P.B.	54.9	.89	10.5	4.1	5.9	0.7	26.5	6.4	5.8	5.0	13.5	1.0
	%	-	1.31	14.6	7.7	11.2	1.3	49.8	11.5	22.6	19.8	52.9	4.4

Table 5

BOUNDARY WATER SURVEY 1954 - 55 LAKE HURON - LAKE ERIE

Organic Components Recovered from Raw Water

CANADA

Sample No.		Total Extract (Chloroform)	Ether Insoluble	Water Soluble	Weak Acids	Strong Acids	Bases	Neutrals	Loss	Neutrals			
										Aliphatic	Aromatic	Oxy.	Loss
	Windsor												
1	P.P.B.	25.4	-	6.1	3.2	2.9	1.4	7.8	4.0	0.5	1.2	6.1	0.0
	%	-		23.8	12.8	11.6	5.4	30.6	15.8	6.4	15.1	78.0	0.5
2	P.P.B.	32.2	-	5.2	1.7	3.1	0.7	16.0	5.5	6.0	4.0	4.5	1.5
	%	-		15.9	5.4	9.8	2.3	49.6	17.0	37.3	25.0	28.4	9.3
3	P.P.B.	33.7	-	9.5	2.5	4.2	2.2	10.8	3.8	1.2	1.8	7.4	0.3
	%	-		28.4	7.6	12.7	6.9	32.2	12.2	11.2	16.9	69.5	2.4
4	P.P.B.	32.0	0.15	7.8	2.3	3.95	1.1	13.1	3.6				
	%	-	0.5	24.3	7.1	12.4	3.5	41.0	11.2				
5	P.P.B.	33.8	0.4	6.8	1.4	2.6	0.7	15.1	6.8	0.5	2.1	10.0	2.5
	%	-	1.4	20.4	3.8	7.5	2.2	44.5	20.2	3.2	13.9	66.0	16.9
6	P.P.B.	23.3	0.65	3.7	3.4	4.9	0.42	7.1	3.2	0.41	0.67	4.9	1.1
	%	-	2.8	15.7	14.8	21.0	1.8	30.3	13.6	5.8	9.5	69.3	15.4
7	P.P.B.	32.7	0.16	5.0	2.6	2.1	2.7	16.9	3.2	0.47	4.4	9.63	2.4
	%	-	0.5	15.3	8.0	6.4	8.4	51.5	9.9	2.8	25.9	57.0	14.3
8	P.P.B.	39.8	-	8.2	2.8	2.7	1.4	18.9	5.8	1.9	1.3	15.0	0.7
	%	-		20.5	7.1	6.8	3.5	47.5	14.6	10.3	6.6	79.1	3.9
	P.P.B.	31.6	0.17	6.5	2.5	3.3	1.3	13.2	4.6	1.6	2.2	8.2	1.2
	%	-	.65	20.6	8.3	11.0	4.3	40.9	14.2	10.8	18.4	3.9	9.2

Table 6

THRESHOLD CONCENTRATIONS* - PPB

	DETROIT				MT. CLEMENS		
	482	492			493		
Lab. No.	Odor	Odor	Taste	Taste + Cl	Odor	Taste	Taste + Cl
Chloroform Extract	150	120	1000	1000	10	150	15
Groups							
Amines	500	340	-	-	100	360	-
Strong Acids	25	34	45	45	100	180	500
Weak Acids	850	410	1440	725	60	410	130
Water Solubles	5000	390	6500	6500	2000	4100	4100
Neutrals	20	36	310	310	15	180	180
Aliphatics	-	-	-	-	-	-	-
Aromatics	-	-	-	-	4	32	20
Oxys	-	115	400	400	40	90	64

*Concentrations are geometric mean of observations of a panel of 3 to 6 persons

Table 7

ODOR ABUNDANCE OF GROUPS*

Sample No.		Water Soluble	Amines	Weak Acids	Strong Acids	Neutrals	Ali-phatics	Aro-matics	Oxys
Detroit 482	Percent Present	54.5	2.2	7.2	6.8	30.5	-	-	-
	Threshold Odor Conc.	5000	500	850	23	19	-	-	-
	Odor Abundance	11	4	8	295	1600	-	-	-
492	Percent Present	43.2	0.9	10.3	10.2	35.3	11	11	78
	Threshold Odor Conc.	390	340	410	34	36	-	-	115
	Odor Abundance	111	3	25	300	980	-	-	678
Mt. Clemens 493	Percent Present	26.7	1.4	6.9	10.9	54.6	24	7	69
	Threshold Odor Conc.	2000	100	60	100	15	-	32	90
	Odor Abundance	13	14	115	109	3640	-	119	420

* ODOR ABUNDANCE = $\frac{\% \text{ of Group Present} \times 1000}{\text{Threshold Odor Concentration in ppb}}$

**Percentages are proportion of neutral group

Directions for the Separation of Carbon Filter Extracts
(To accompany Separation Chart)

General:

One half to one gram of sample of extract is desirable for the separation but this amount is not always available. As little as 0.2 grams can be used although final yields may be less accurate than with the larger amounts. The sample should be virtually free of the solvent used in extracting the carbon (usually chloroform) although it is not practicable to remove the last traces without risking loss of other components.

Step 1 -

Dissolve as much of the extract as possible in diethyl ether (1). Use several small portions of solvent if necessary. Decant or filter if necessary, collecting the ether in a separatory funnel. (Warning: AVOID THE USE OF SILICONE STOPCOCK GREASE OR OTHER SOLUBLES IN ALL OPERATIONS. USE STOPCOCKS DRY OR USE FUNNELS WITH TEFLON FITTINGS.)

Step 2 -

The residue from (1) (in some cases all of the original material will go into the ether) is dissolved in a small amount of 95 percent ethyl alcohol (3). Water is added followed by extraction with ether. If a precipitate forms (6) it is filtered, dried and weighed. This is the WATER AND ETHER INSOLUBLE GROUP (A). Save the ether layer (5) and the water layer (4).

Step 3 -

Extract ether solution (1) with water (7). Combine the water layers (8) and (4), evaporate, dry and weigh. This is the WATER SOLUBLE GROUP (B). Low heat should be used in all drying operations. A water bath is satisfactory for this purpose. Combine ether layers (10) and (5).

Step 4 -

Extract ether layers (10) and (5) with 5 percent hydrochloric acid (11). Separate the phases. Make the water layer (13) basic (pH 10-11) with 5 percent NaOH (15) and extract with ether. Dry the ether solution (18) with sodium sulfate (overnight, if time allows), filter, evaporate and weigh. This is the AMINE GROUP (C). The water layer (17) is discarded unless it is desired to recover the amphoteric compounds. These compounds are not considered significant for most studies.

Step 5 -

Ether layer (12) is extracted with 5 percent NaOH (14). Save the ether layer (19). The water layer (20) is saturated with CO_2 by bubbling the gas through the solution for 30 minutes or more (22). This solution is extracted with ether followed by drying, filtering, evaporation and weighing (24). This is the WEAK ACID AND PHENOL GROUP (E).

Step 6 -

Water layer (25) is acidified with 5 percent HCl (26), extracted with ether, dried, evaporated and weighed. This is the STRONG ACID GROUP (F).

Step 7 -

Ether layer (19) is dried, filtered, evaporated and weighed. This is the NEUTRAL GROUP (D)

Step 8 -

The NEUTRAL GROUP (D) is chromatographed into aliphatic, aromatic and oxy fractions as follows: Silica Gel (Davison Code 950) is tamped to a height of 10 cm. in a glass column 19 mm. in diameter. This requires 18 gms. of Silica Gel. The adsorbent is wetted with the first solvent 2,2,4-trimethylpentane ("isooctane"); the required volume is 17 ml. Five times this volume, 85 ml. of each solvent is used in subsequent elutions.

A sample not exceeding 1.5 gms. is dissolved in 4 ml. of isooctane and adsorbed on top of the column. The remainder of the 85 ml. of solvent is percolated through the column. The effluent, containing the aliphatic hydrocarbon fraction is collected in a tared flask, the solvent removed and the weight recorded. In a similar manner the aromatic fraction is eluted with benzene and the oxy (polar) fraction with a mixture of equal volumes of chloroform and methanol.

SEPARATION OF CARBON FILTER EXTRACT

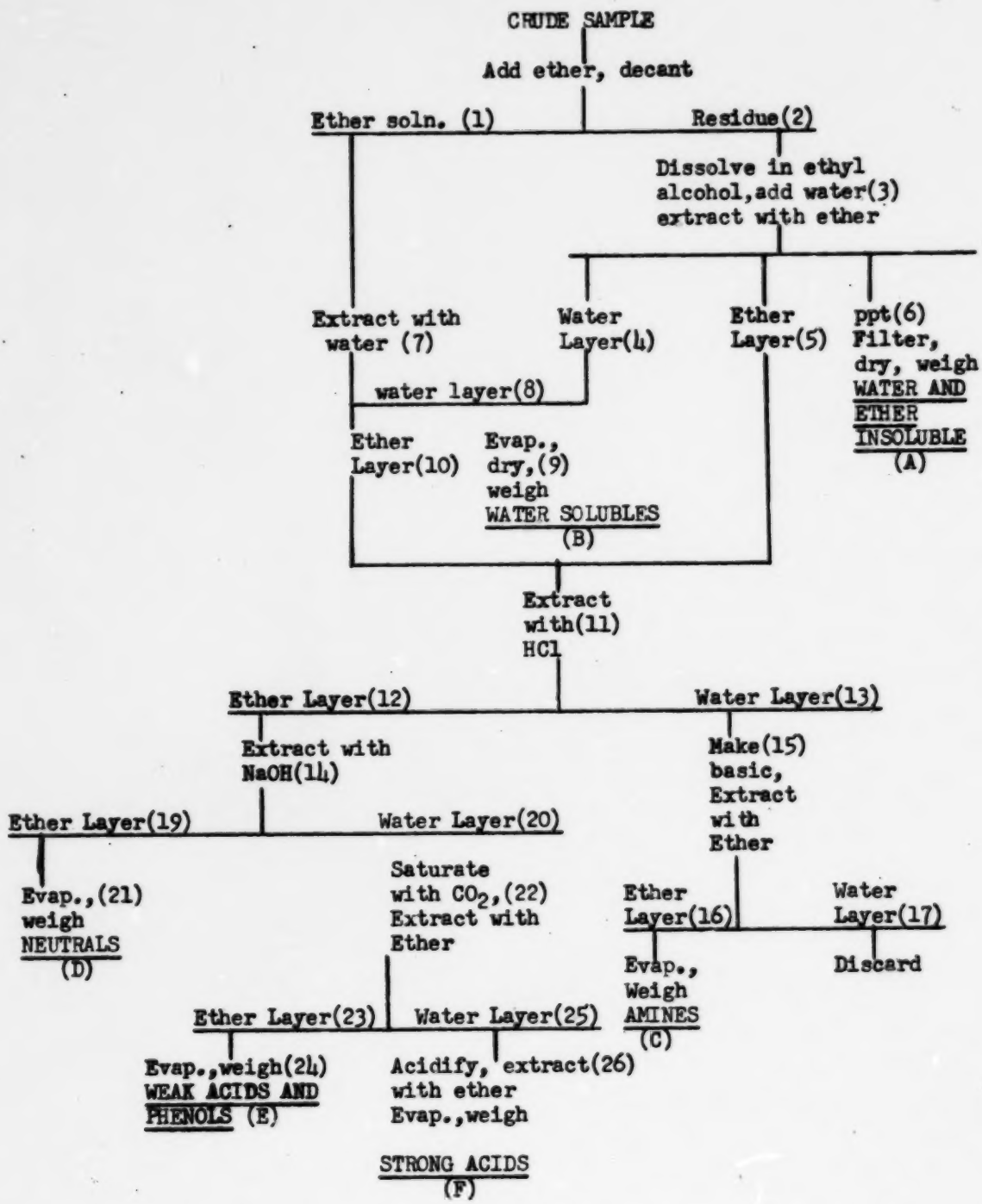

TABLE A-1

CARBON FILTER STUDIES - PORT HURON, UTICA, SAGINAW, BAY CITY, AND DETROIT

City	Dates of Operation From	To	Lab. No.	Gallons of Water Filtered	Filter No.	DDT Present Yes	No	Organic Materials Raw Water Grams	Finished Water Grams	Recovered Parts Per Billion
Port Huron	5-18-53	6-12	417	4,400	I	X		11.1		670
					II	X		14.72		880
Port Huron	9-10	10-20	428	6,300	I		X	.81		34
				5,450	II		X		.33	16
Utica	5-1	6-11	418	No Record	I	X		7.6	-	-
					II	X		1.6	-	-
Utica	6-3	6-18	419	500	I		X		0.58	31
					II		X		5.74	302
SAGINAW Midland Booster Station	9-11	10-20	431	8,240	I		X	.90		29
Saginaw	9-11	10-20	430	8,810	I		X		0.82	25
Detroit	11-14-51	11-26-41	-	6,960	-		X	.34		13
Bay City	9-11	10-16	429	No Record	I		X	0.8		-
					II		X		.37	-
Detroit	9-21	10-21	432	No Record	I		X	1.2		-
					II		X		.63	-

TABLE A-2

CARBON FILTER STUDIES - MT. CLEMENS, MICHIGAN

Dates of Operation From	To	Lab. No.	Gallons of Water Filtered	Filter No.	DDT Present Yes	DDT Present No	Organic Materials Recovered Raw Water Grams	Organic Materials Recovered Finished Water Grams	Organic Materials Recovered Parts Per Billion
3-19-51	5-51	433	18,860	-		X	6.1		85
		433	75,200	-		X		2.72	9.6
2-2-53	3-2	392	6,830	I	X		17.6		680
				II		X	1.20		46
3-9	4-6	410	1,650	I	X		4.5		717
				II	X		1.3		296
3-9	4-30	411	9,670	I	X			4.0	108
				II		X		4.5	122
4-6	4-30	412	3,930	I	X		4.4		293
		412	561	IIA	X		.83		392
		412	3,373	IIB	X		3.82		299
5-1	5-13	413	No flow	I	X		10.1		-
				II	X		5.2		-
4-8	5-12	414	5,900	I	X			5.27	236
				II	X			2.90	130
9-17	10-21	427	2,460	I		X		0.4	44
				II		X		1.19	58

* Filter system consisted of Cliffchar 4-10 mesh filter (I) followed in series with Nuchar C-190 (II) filter.

TABLE A-3

CARBON FILTER STUDIES - WYANDOTTE, MICHIGAN

Dates of Operation 1953 From	To	Lab. No.	Gallons of Water Filtered	Filter No.	DDT Present Yes	DDT Present No	Organic Materials Recovered Raw Water Grams	Finished Water Grams	Parts Per Billion
1-29	2-12	383	5,245	I	X		2.95		147
				II		X	.34		17
1-29	2-11	385	5,430	I	X			.24	12
				II		X		1.30	63
2-26	3-6	390	2,910	I	X		4.58		416
				II		X	.83		75
2-26	3-6	391	3,215	I	X			4.46	366
				II		X		.85	70
3-11	3-23	393	4,430	I	X		4.86		290
				II	X		1.19		71
3-11	3-23	394	4,810	I	X			3.74	205
				II	X			2.8	153
10-30	11-16	426	4,120	I		X	0.7		45
				II		X		1.2	65
1-13-54	1-31	441	3,311	I		X	2.06		165
			4,570	II		X		1.83	104
2-1-54	2-11	448	3,219	I		X	1.57		129
			3,475	II		X		1.62	124

Note: Nos. 383 thru 394 collection system consisted of a granular carbon (Cliffchar 4-10) filter followed in series by a c-190 (Nuchar) filter. Nos. 426-448 consisted of single filters of mixed Cliffchar and C-190.

RESULTS OF GROUP SEPARATIONS ON ORGANIC EXTRACTS
FROM VARIOUS WATER SUPPLIES-BOUNDARY WATERS

	Percent of Total Recovery						
Type of Water	Raw	Raw	Wyandotte Raw	Fin.	Raw	Mt. Clemens Raw and Fin.	Detroit
Sample No.	393-1	441-1	448-1	448-2	392-1	414-1+II	**
Ether Insolubles	-	-	1.2	3.2	-	-	-
Water Solubles	-	7.7	5.9	15.6	-	2.2	46
Amines	.2	1.1	2.4	4.8	0.3	1.6	1
Neutrals	61	57	46.0	21.4	89.2	61.5	45
Aromatics	(63)*	-	-	-	(56.1)	(66.3)	-
Aliphatics	(21)*	-	-	-	(17.3)	(24.2)	-
"Oxy"	(5)*	-	-	-	(3.0)	(9.0)	-
Weak Acids and Phenols (1)	0.6	0.8	-	-	2.2	16.9	6
Weak Acids and Phenols (2)	-	-	25.4	21.6	-	-	-
Strong Acids	1.0	2.1	3.4[a]	10.0[a]	.05	12.1	6
Aldehydes	0.2	-	-	-	0.6	0.2	1
Total Recovery	63.5	68.6	84.3	76.6	92.3	94.5	105

*Percent of neutrals

**Sample collected and extracted by Detroit - Run Nov. 14-26, 1951

TABLE A-5